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(54) PLAYBALLS

(71) We, THE DUNLOP RUBBER COMPANY LIMITED, a British Company of Dunlop House, Ryder Street, St. James's, London, S.W.1. (formerly of 1 Albany Street, London, N.W.1.), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to performed, to be particularly described in and by the following statement:—

This invention relates to playballs, particularly golf balls, and to processes for pro-

ducing them.

The conventional golf ball designed for tournament play is usually a ball of excellent quality and is generally accepted by professional and other serious golfers as being superior to other types of construction. However, the production of such balls is an expensive matter in view of their complex structure involving the winding of a considerable length of elastic rubber thread about an inner core which in the best quality ball consists of a sac containing a liquid composition necessitating freezing to permit satisfactory winding of the thread. As a consequence of this and other difficulties of manufacture, balls of tournament quality are expensive and there is a demand for a simpler, cheaper type of ball which would satisfy many golfers and would be satisfactory for use on driving ranges. There have been numerous proposals for moulding golf balls from a homogeneous composition into what are generally referred to as 'solid moulded balls' or single component balls. Although such balls can be produced very cheaply, in general they suffer from the serious defect of susceptibility to cracking and subsequent disintegration during play. Various measures have been proposed to mitigate these disadvantages but at present solid moulded balls are not generally acceptable to serious golfers.

We have now found that golf balls of very good quality can be obtained by making use of simple moulding techniques but having a separate cover for the ball.

Accordingly, in one aspect the present in-

vention provides a playball, especially a golf ball, having a core surrounded by a cover, the core comprising a material formed from an elastomer by highly cross-linking the elastomer with flexible cross-links by means of a cross-linking agent which is used in an amount from 20—75% by weight of the elastomer. The invention is described below with particular reference to golf balls. It has been found that golf balls according to this invention have excellent qualities, being comparable to balls of tournament quality produced by the conventional process involving winding an elastic thread about an inner core.

The golf balls of this invention possess a marked advantage over golf balls moulded wholly from a highly cross-linked elastomer without a separate cover. The latter balls are subject to splitting and disintegration in use and therefore the properties of the ball have to be specially adapted to avoid this disadvantage with the consequence that often certain optimum properties, such as resilience, have to be sacrificed to dimensional stability. In the balls of this invention, on the other hand, the optimum resilience can be utilised because the cover precludes disintegration of the core.

The core elastomer of the balls of this invention can be any material capable of being cross-linked. In particular, it can be a polymer or copolymer of butadiene or isoprene, for example cis-polybutadiene (having for instance a cis-polymer content of at least 50% by weight), or trans-polyisoprene or trans-polybutadiene (having for instance a trans-polymer content of at least 90% by weight). Examples of other suitable elastomers are copolymers of styrene and butadiene, polymers and copolymers of ethylene and propylene, polysulphides, natural rubber and butyl rubber.

The term "copolymer" used in this specification includes polymers obtained from two, three or more reactants, (which can be monomers, oligomers or other partially polymerised materials), inter polymers, block polymers, and blends thereof.



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The cross-links in the core can be obtained, for example by use of a cross-linking agent, conveniently a monomeric substance, for example a di-functional compound, having readily polymerisable groups which will readily link with the elastomer. Examples of suitable cross-linking agents are unsaturated esters of di-carboxylic acids, the unsaturation being in either the acid or alcohol moiety, or both. Very suitable cross-linking agents are esters of acrylic or methacrylic acids, for instance trimethylolpropane trimethacrylate, which is the ester derived from three molecules of methacrylic acid and one molecule of trimethylolpropane (i.e. 1,2,3-hydroxymethylpropane). The amount of cross-linking agent used is that sufficient to give highly cross-linked material. This is generally in the range of 20-75% (especially 30-60%) of the weight of the elastomer. There is preferably polymerisation between adjacent molecules of the cross-linking agent so that the cross-links formed between molecules of the elastomer contain at least a proportion of chains formed by polymerisation of molecules of the cross-linking agent.

The elastomer used for the core of the golf ball of this invention preferably contains a filler, for example silica or titanium dioxide or a lead compound. However, any filler can be used provided it is dense enough to give the desired weight of ball and is compatible with the other ingredients. The amount of filler will depend upon the nature of the other ingredients but will generally be in the range of 30-80% by weight of the elastomer, for example 50-70% by weight.

The material used for the cover of the balls of this invention can be of the same or different material as the core. Thus, it can be a highly cross-linked elastomer with flexible cross-links or it can be any of a wide range of materials. For example, the cover can be of one or more of the following: - balata; trans-polymers of a conjugated diolefine, for instance trans-polyisoprene or trans-polybutadiene (preferably having a trans-polymer content of at least 90%); cis-polymers of conjugated diolefines, for instance cis-polyisoprene or cis-polybutadiene (preferably having a cispolymer content of at least 50%); polyurethanes; polyamides; copolymers of butadiene and styrene; polymers and copolymers of ethylene or propylene; copolymers of unsaturated olefines with esters of unsaturated acids, 55 for instance methyl methacrylate-butadiene copolymers, especially those of high (especially predominating) methyl methacrylate content; neoprene, especially in crystalline form; copolymers of ethylene and unsaturated carboxylic acids, for instance ethylene-acrylic acid and ethylene-methacrylic acid copolymers such as the metal-containing copolymers of our U.K. Application No. 38674/65 (Serial No. 1,148,529). If desired blends of two or more substances can be used, for example a blend

of cis-polybutadiene and an ethylene-methacrylic acid copolymer.

The cover composition can contain a filler, for example inorganic fillers such as silica, lead carbonate or titanium dioxide, the latter being especially useful in providing a white appearance to the ball.

A further form of golf ball according to the present invention is one in which the core itself consists of two or more portions. Such a structure is very useful where it is wished to concentrate the weight of the ball in the centre, though it can be used in other circumstances. In such a structure the core can consist of a spherical inner core portion (for instance a steel or glass ball) surrounded by one or more outer core portions which provide a spherical shell about it. For example, if there are two outer portions they can be in the form of hollow hemi-spherical shells which together surround the inner core to form a composite structure of spherical shape. The material composing the inner core and outer core can be the same or different. One or more of the inner core and outer core portions can comprise a cross linked elastomer of the sort referred to above.

The cross-linking is conveniently promoted use of a free radical polymerisation initiator, for instance a peroxide catalyst such

as dicumyl peroxide.

The golf ball of the present invention can be made by blending together an intimate mixture of the elastomer and cross-linking agent and, where appropriate, the polymerisation initiator and filler, and moulding the mixture 100 in a spherical mould. It is convenient that the moulding conditions are such as to lead to the desired cross-linking of elastomer with crosslinking agent. However, if desired the crosslinking reaction can be carried out (or at least 105 completed) in a separate step from the moulding step.

The method by which the cover is applied to the core depends upon the nature of the material used for the cover. Where it is a thermoplastic material it can be applied either by an injection moulding process in which molten material is forced around the periphery of the core centrally mounted in a spherical mold. Alternatively, it can be applied in the 115 form of two hemi-spherical shells encasing the core, which when subjected to moulding conditions are moulded to the core and sealed together along their edges to form a smooth integral spherical shell cover.

The means by which the cover is fixed to the core depends very much upon the nature of material of the cover and core. Where the cover is formed by a process of injection moulding around the core there is normally no need for auxiliary means of fixing as the material of the cover will, while still molten, flow into intimate contact with the periphery of the core resulting in a strong bond between them. However, where the cover is applied, for 130

example by compression moulding using two hemi-spherical shells it may be necessary to use auxiliary means for fixing, for example an adhesive. An alternative auxiliary mean of fixing is by mechanical interlocking means, for example by forming the core so as to have

protuberances or recesses in its surface onto which the cover can lock when moulded onto the core.

The dimensions of the components of a golf ball according to the present invention may, for example, be as follows:—

Ball Diameter	1.62 inches	1.68 inches
Two Component Ball:		
Core Diameter	0.75-1.6 inches	0.75—1.64 inches
(preferred range)	1.00-1.54 inches	1.00—1.60 inches
Cover thickness	0.020—0.435 inch	0.020—0.465 inch
preferred rang	0.040-0.310 inch	0.040-0.340 inch
particularly preferred range	0.060-0.125 inch	0.060-0.25 inch
Three Component Bali		
Inner Core Diameter	0.25-1.00 inch	0.25100 inch
Overall Core Diameter	0.75—1.60 inches	0.75-1.64 inches
Cover Thickness	As for two component ball	

This invention is illustrated by the following Examples in which the parts referred to are
parts by weight. In all the examples a 20%
w/w solution of triphenyl methane triisocyanate in methylene chloride was used as
the adhesive between the core and cover in
the case of two components and between
each of the core components and between the

core and cover in the case of multi-component balls except where otherwise stated (see Example 11).

Example I

A spherical core of 1.48 inches diameter was compression moulded from the following composition and cured in the mould for 20 minutes at 150°C.

Parts
100
40
20
5
40
3

The core had a Shore C Hardness of 88.

A cover compound was prepared by blending together:

Parts
50
50
40
4
3.15

The ethylene-methacrylic acid copolymer had a melt flow index of 0.5 gram/10 minutes as determined by B.S. 2782 Method 105C and contained 7% by weight of methacrylic acid of which 80% was present in the copolymer in the form of the sodium salt. The cis-polybutadiene contained 97% cis-1,4 units and had a Mooney viscosity (ML-4) at 100° of 50.

Half shells (i.e. hollow hemispheres) 0.070

Half shells (i.e. hollow hemispheres) 0.070 inch thick and of internal diameter 1.48 inches were preformed by compression moulding the cover compound at 100°—120°C., fitted around the core coated with adhesive, assembly moulded into a composite ball, and cured in a dimpled 1.632 inches diameter mould for 30 minutes at 160°C. followed by 10 minutes cooling prior to extraction from the mould.

The golf ball thus obtained had a weight of 45.2 grams and a diameter of just less than 1.62 inches. This ball was subjected to comparative tests in which it was compared with:

(A) a high quality tournament golf ball, (B) a conventional practice ball and (C) a solid moulded (i.e. single component) moulded ball based on a composition similar to that of the

core of the ball of this Example. The cutting resistance in play and flight characteristics of the four balls are shown in Tables I and II below.

The tournament golf ball (A) had been made as follows:

A core centre of rubber paste contained in a rubber sac and having a diameter of 1.05 inches was thread-wound to yield a core of diameter 1.56—1.58 inches. A cover of a composition of trans-polyisoprene of thickness 0.040 inch was moulded onto the core to provide a ball having a diameter of 1.620 inches and a weight of 45.02 grams.

The conventional practice ball (B) has essentially the same construction as the tournament ball, except that it had a solid rubber corecentre of 1.25 inches diameter and a cover of a crystalline polychloroprene composition. The ball had a diameter of 1.618 inches and weighed 45.3 grammes.

The single component ball (C) was made by moulding the composition detailed below and curing for 30 minutes at 160°. 30

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	Parts
Cis-polybutadiene	100
Tri-methylolpropane tri-methacrylate	40
Silica	35
Lead carbonate	28
Titanium dioxide	5
Dicumyl peroxide	3

In Table 1 the following abbreviations are used:—

CR (b) = cutting resistance of the ball; H = Hardness (Shore C);

Rebound = % rebound from a height of 100 inches

Resilience = coefficient of restitution determined by firing a projectile at a ball and noting the time taken for the ball and projectile to travel a predetermined distance.

travel a predetermined distance. In Table II "Click" is the sound made by contact between the golf club and the ball, "Carry" is the distance travelled by the ball before bouncing.

"Total flight" is the total distance travelled by the ball and "Trajectory" is measured on an arbitrary scale for comparing the heights to which balls rise during flight, a higher figure indicating a higher flight path.

indicating a higher flight path.

Examples 2—9 describe other two-component golf balls whose properties have been compared with balls A, B and C of Example 1, as shown in Tables I and II.

Example 2

A spherical core of 1.48 inches diameter was moulded as in Example 1.

A cover compound was prepared by blending together:

	Parts
*Ethylene-methacrylic acid copolymer	100
Titanium dioxide	5
Lead carbonate	15

^{*}The copolymer was that used in Example 1.

Half shells 0.070 inch thick and of internal diameter 1.48 inches were formed by compression moulding at 120—140°C. They were fitted around a core identical with that of Example 1 and the assembly was compression moulded into a composite ball for 15—20 minutes at 160°C. followed by 10 minutes cooling before extraction of the ball from the

mould. The resulting golf ball had a weight 40 of 45.4 grams.

Example 3

A spherical core of 1.48 inches diameter was compression moulded from the following composition and cured in a mould for 20 minutes 45 at 150°C.

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	Parts
Cis-polybutadiene	100
Trimethylol propane trimethacrylate	40
Silica	35
Lead carbonate	45
Titanium dioxide	5
4,4'-thiobis (6-tert-butyl-metacresol)	0.5
Dicumyl peroxide	3

The core had Shore C hardness of 80 and weighed 37.9 gram.

Half shells (i.e. hollow hemispheres) 0.070 5 inch thick and of internal diameter 1.48 inches were injection moulded at 220°C. from an ethylene methacrylic acid copolymer.

The half shells were fitted round the core coated with adhesive and the assembly was 10 moulded into a composite ball in a hot dimpled 1.64 inches diameter mould for 5 minutes at 160°C. followed by 15 minutes cooling prior to extraction from the mould. The resultant ball had a weight of 45.9 gram.

EXAMPLE 4

A spherical core was prepared in the same way and using the same compound as in Example 3.

Half shells of the same dimensions as in Example 3 were injection moulded at 180°C from a Thermolastic 266 thermoplastic block copolymer of styrene and butadiene.

The half shells were fitted round the core coated with adhesive and the assembly was moulded into a composite ball in a hot dimpled 1.64 inches diameter mould for 5 minutes at 140°C followed by 15 minutes cooling prior to extraction from the mould. The resultant ball had a weight of 46.0 grams.

Example 5

A spherical core was prepared in the same way as in Example 1 but using the following compound.

Parts
100
40
25
36
5
0.5
3

The core had a Shore C hardness of 76 and weighed 35.8 gram.

Half shells of the same dimensions as in Example 3 were injection moulded at 200°C using a 50/50 tumbled mix blend of an acrylonitrile - butadiene - styrene terpolymer (known as Cycolac H, and a thermoplastic polyurethane polymer (known as Texin 192/A).

The half shells were fitted round the core

with adhesive and the assembly was moulded 45 into a composite ball in a hot dimpled 1.64 inches diameter mould for 5 minutes at 160°C followed by 15 minutes cooling prior to extraction from the mould. The resultant ball had a weight of 45.9 grams.

Example 6

A spherical core was prepared in the same way as in Example 1 but using the following compound.

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	Parts
Cis-polybutadiene	100
Trimethylol propane trimethacrylate	40
Silica	25
Lead carbonate	40
Titanium dioxide	5 .
4,4'-thiobis (6-tert-butyl-metacresol)	0.5
Dicumyl peroxide	3

The core had a Shore C hardness of 74 and weighed 36.7 grams.

Half shells of the same dimensions as in 5 Example 3 were injection moulded at 200°C using a 75/25 blend of an ethylene methacrylic acid copolymer and cis-polybutadiene; prepared by Banbury mixing at 145°C, followed by chipping the cooled stock. The ethylene methacrylic acid copolymer and the cis-polybutadiene were the same as in Example

The half shells were fitted round the core and the assembly moulded into a composite ball in a hot dimpled 1.64 inches diameter mould for 5 minutes at 160°C followed by 15 minutes cooling prior to extraction from the mould. The resultant ball had a weight of 45.9 grams.

Example 7

A spherical core was prepared in the same way as in Example 1, but using the following compound.

	Parts
Cis-polybutadiene	100
Trimethylol propane trimethacrylate	40
Silica	35
Lead carbonate	· 55
Titanium dioxide	5
4,4'-thio bis (6-tert-butyl-metacresol)	0.5
Dicumyl peroxide	3

25 The core had a Shore C hardness of 78 and weighed 38.1 grams.

Half shells of the same dimensions as in Example 3 were injection moulded at 190-200°C using an ethylene-vinyl acetate copolymer. The copolymer contained 18% of vinyl acetate and had a melt flow index of 2.5 grams/10 minutes as determined by BS.2782 method 105C.

The half sheets were fitted round the core coated with adhesive and the assembly was moulded into a composite ball in a hot dimpled 1.64 inches diameter mould for 5 minutes at 150°C followed by 15 minutes cooling prior

to extraction from the mould. The resultant ball had a weight of 46.2 grams.

EXAMPLE 8

A spherical core was prepared in the same way as in Example 1 but using the compound of Example 7.

Half shells of the same dimensions as in 45 Example 3 were injection moulded at 2100-220°C from a low density polyethylene homo-polymer having a melt flow index of 20 grams/10 minutes as determined by BS.2782 method 105C.

The half shells were fitted round the core

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and the assembly was moulded into a composite ball in a hot dimpled 1.64 inches diameter mould for 5 minutes at 160°C. followed by 15 minutes cooling prior to extraction from the mould. The resultant ball had a weight of 45.2 grammes.

EXAMPLE 9 A spherical core was prepared in the same way as in Example 1, but using the following compound.

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	Parts
Cis-polybutzdiene	100
Trimethyl propane trimethacrylate	30
Silica	20
Lead carbonate	25
Titanium dioxide	5
4,4'-thio-bis (6-tert-butyl metacresol)	0.8
Dicumyl peroxide	3.15

The core had a Shore C hardness of 70, and was 34.0 grammes in weight.

Half shells were compression moulded in

a cold mould using a polyethylene liner from 15 the following composition:

	Parts
Cis-polybutadiene	100
Trimethylol propane trimethacrylate	40
Silica	35
Lead carbonate	28
Titanium dioxide	5
4,4'-thio-bis (6-tert-butyl metacresol)	0.8
Dicumyl peroxide	3.15

The half shells were fitted round the core coated with adhesive and the assembly was moulded into a composite base in a hot dimpled 1.64 inches diameter mould for 20 minutes at 150°C. followed by 15 minutes cooling prior to extraction from the mould. The resultant ball had a weight of 45.1 grammes. 25

EXAMPLE 10

This Example describes a four-component

ball in which the core consists of an inner core surrounded by two co-operating annular half shells, the whole being encased in a cover. The balls of Example 10 and Example 11 are compared with balls A, B and C in Tables I and II.

A spherical core of 1.0 inch diameter was compression moulded and cured as in Example 35 1, but using the following compound.

	Parts
Cis-polybutadiene	100
Trimethylol propane trimethacrylate	40
Silica	20
Lead carbonate	35
Titanium dioxide	5
Dicumyl peroxide	3

Annular half shells of internal diameter 1.0 inches and outside diameter 1.48 inches were compression moulded in a cold mould using

a polyethylene liner from the following com- 5 position:

	Parts
Cis-polybutadiene	100
Trimethylol propane trimethacrylate	30
Silica	20
Lead carbonate	25
Titanium dioxide	5
4,4'-thio-bis (6-tert-butyl metacresol)	0.8
Dicumyl peroxide	3.15

Cover half shells as in Example 6 but of a 50/50 blend of the same ethylene methacrylic acid copolymer and cis-polybutadiene were then obtained by injection moulding at 100°C. using stock tumble mixed with 3 percent of dicumyl peroxide.

The annular half shells were then fitted around the core coated with adhesive. The core assembly was then treated with adhesive and the cover half shells fitted around it. The whole assembly was then moulded into a com-posite ball in a hot dimpled 1.64 inches diameter mould for 20 minutes at 150°C. followed by 15 minutes cooling prior to extraction from the mould.

The resultant ball had a weight of 46.0 grammes.

EXAMPLE 11

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This Example described a second four-component ball.

Inner annular half shells of internal diameter 0.25 inches and of external diameter 1.0 inches were compression moulded from the following composition in a cold mould using a polyethylene liner.

Parts
100
35
20
25
5
3

Outer annular half shells of internal diameter 1.0 inches and outer diameter 1.48 inches diameter were compression moulded

from the following composition in a similar way to the above.

	Parts
Cis-polybutadiene	100
Trimethylol propane trimethacrylate	3)
Silica	20
Lead carbonate	15
Titanium dioxide	5
4,4'-thio-bis (6-tert-butyl-metacresol)	0.8
Dicumyl peroxide	3.

The inner annular half shells were fitted around a 0.250 inch diameter unpolished rough surface steel ball bearing coated with a layer of Chemlok 216 adhesive and the assembly was cured for 10 minutes at 150°C in a plain surfaced mould and cooled for 10 minutes prior to extraction. This ball of 1.0 inches diameter was then buffed with abrasive paper and coated with the same adhesive. The outer annular half shells were then fitted around this assembly and cured for 20 minutes at 150°C in another plain surface mould. The

mould was cooled prior to extraction. The cured core assembly of 1.48 inches diameter was then buffed with abrasive paper and again coated with adhesive. Cover half shells as in Example 7 were fitted to the core and this assembly moulded in a hot dimpled 1.64 inches diameter mould for 5 mins, at 150°C. followed by 15 minutes cooling prior to extraction from the mould.

The resultant ball had a weight of 45.9 grammes.

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			TABLE I		
	Ball	CR(b)	Н	Rebound	Resilience
	A	Very Good	70	68	0.710
	В	Good	70	60	0.550
	С	Good	73	68	0.590
	Example 1	Very good	72	67	0.660
	Example 2	Excellent	80	68	0.677
	Example 3	Excellent	89	69	0.663
	Example 4	Fairly good	48	62	0.639
	Example 5	Very good	88	69	0.630
	Example 6	Very good	79	68	0.660
	Example 7	Very good	61	71	0.623
	Example 8	Very good	75	69	0.627
	Example 9	Good	68	66	0.683
	Example 10	Good	67	68	0.625
	Example 11	Very good	61	67	0.610
-			TABLE II		······································
	Ball	"Click"*	Carry (yds)	Total Flight (yds)	Trajectory
•	A	Very good	235	258	283
	В	Good	175	226	· 21½
	С	Good	201	243	211
	Example 1	Very good	223	237	26 <u>₹</u>
	Example 2	Very good	225	240	22
	Example 3	Slightly hard	219	247	26 <u>1</u>
	Example 4	Good	204	243	23
	Example 5	Very good	215	249	26
	Example 6	Very good	219	246	27
	Example 7	Very good	200	230	23 1
	Example 8	Very good	213	239	25 1
	Example 9	Very good	224	247	27
	Example 10	Very good	200	230	23 1
	Example 11	Very good	189	229	221

It will be seen from the results in Tables I and II that, considering flight characteristics or resistance to cutting balls of these Examples resemble the tournament ball to a greater extent than either the conventional practice ball of the single component ball.

WHAT WE CLAIM IS: -

1. A playball having a core surrounded by a cover, the core comprising a material formed from an elastomer by highly cross-linking the elastomer with flexible cross-links by means of a cross-linking agent which is used in an amount from 20 to 75% by weight of the elastomer.

2. A playball according to Claim 1, which is a golf ball.

3. A golf ball according to Claim 2, in which the core is a single moulding.

4. A golf ball according to Claim 2 or 3, in which the core elastomer comprises a polymer or copolymer of butadiene or isoprene.

5. A golf ball according to Claim 4, in which the core elastomer is cis-polybutadiene, trans-polyisoprene or trans-polybutadiene.

A golf ball according to any of Claims
 to 5, in which the flexible cross-links are provided by a difunctional ester of acrylic or methacrylic acid.

7. A golf ball according to Claim 6, in which the difunctional ester is tri-methylolpro-

pane trimethacrylate.

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8. A golf ball according to any of Claims 2 to 7, in which the core comprises a spherical inner core surrounded by an annular outer core.

9. A process for the manufacture of a golf ball according to Claim 2, in which an intimate blend of a cross-linkable elastomer, a cross-linking agent and a filler are moulded into a golf ball core, the core is cured under the influence of an initiator for the cross-linking reaction between the elastomer and cross-linking agent, and a cover for the ball is formed around the cured core.

10. A process according to Claim 9, in which the amounts of cross-linking agent and of filler are respectively 30—60% and 50—

70% by weight of the elastomer.

11. A process according to Claim 9 or 10, in which the cross-linking agent is trimethylol-propane trimethacrylate.

12. A process according to Claim 9, 10 or 11, in which the filler comprises a mixture of a lead compound and titanium dioxide.

13. A process for the manufacture of a golf ball according to Claim 2, substantially as described herein.

14. A golf ball obtained by the process of any of Claims 9 to 13.

15. A golf ball according to Claim 2, substantially as described herein.

16. A golf ball according to Claim 2, substantially as described in Example 1 or 2.

17. A golf ball according to Claim 2, substantially as described in any of Examples 3 to 11.

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